

Organometallic Complexes of Rhodium (1) ligated by Heterocyclic Thioamides

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Abstract

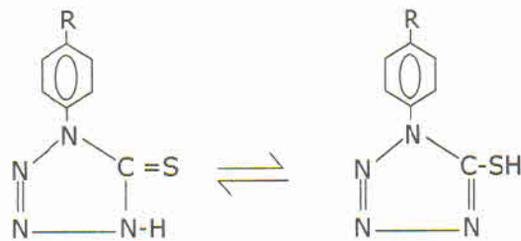
Organometallic derivatives of rhodium(1) of the type $[\text{RhX}(\text{P}\phi_3)_2(\text{ligand})]$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NCS}^-$ & SnCl_3^-), $[\text{Rh X}(\text{P}\phi_3)(\text{CO})(\text{ligand})]$ ($\text{X} = \text{Cl}^-/\text{Br}^-$) and $[\text{Rh}(\text{P}\phi_3)_2](\text{Py})(\text{ligand})\text{BF}_4$ have been synthesized using $[\text{Rh}(\text{P}\phi_3)_3]$ ($\text{X} = \text{Cl}^-/\text{Br}^-$) as precursor and parachloro, paramethyl, paramethoxy and Para ethoxy derivatives of 1-phenyl tetrazoline-5-thione as ligand. The oxidation state of rhodium in compounds was verified by titrating with ceric ammonium sulphate using ferroin as indicator. All four coordinated compounds are isostuctural with square planar precursor indicated by various physico-chemical data.

Key words : Organorhodium (1), Thioamides, Wilkinson Catalyst.

Introduction

The phosphine complexes of rhodium(1) are versatile catalyst for hydrogenation¹ and hydroformylation² reactions. This concomitant paper comprises a resurrence of our interest in the synthesis and spectral characterization of rhodium(1) complexes ligated by heterocyclic thioamides using wilkinson catalyst² as precursor complex. Some solid and stable para substituted phenyl derivatives of 1-substituted tetrazoline-

5-thione are used as ligands (Str. 1).



($\text{R} = \text{CH}_3-, \text{Cl}, \text{CH}_3\text{O}-; \text{CH}_3\text{CH}_2\text{O}-$)
(Str. -1)

Experimental

All chemicals used were either of Anala R or chemically pure grade. The ligands, 1-paratolyl tetrazoline-5-thione (1ptT5TH), 1-paramethoxy phenyl tetrazoline-5thione (1PMPT5TH) and 1-Paraethoxy phenyl tetrazoline-5-thione (1PEPT5TH) were prepared by the method reported in literature³. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was obtained from Johnson Matthey Ltd. and triphenyl phosphine ($\text{P}\phi_3$) from Albright and Wilson Ltd. and their purity was checked.

Preparation of complexes :

$[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{ligand})]\text{BF}_4$ was prepared following our previous method reported in literature⁴.

Sl. No. 1: $[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{P-CH}_3\text{-L})]\text{BF}_4$:

(MF = $\text{RhC}_{49}\text{H}_{43}\text{N}_5\text{P}_2\text{S BF}_4$)
 Found (%) : C = 60.11; H = 4.38; N = 7.01;
 Rh = 10.35
 Calculated(%) : C=59.71; H = 4.36; N = 7.10;
 Rh = 10.45

Sl. No. 2 : $[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{P-CH}_3\text{O-L})]\text{BF}_4$:

(MF = $\text{RhC}_{49}\text{H}_{43}\text{N}_5\text{OP}_2\text{S BF}_4$)
 Found (%) : C = 58.78; H = 4.39; N = 7.02;
 Rh = 10.32
 Calculated(%) : C=58.71; H = 4.29; N = 6.99;
 Rh = 10.29

Sl. No. 3 : $[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{P-CH}_3\text{CH}_2\text{O-L})]\text{BF}_4$:

(MF = $\text{RhC}_{50}\text{H}_{45}\text{N}_5\text{OP}_2\text{S BF}_4$)

Found (%) : C = 59.11; H = 4.48; N = 6.99;
 Rh = 10.32
 Calculated(%) : C=59.12; H = 4.43; N = 6.89;
 Rh = 10.14

Sl. No. 4: $[\text{Rh}(\text{P}\phi_3)_2(\text{Py})(\text{P-Cl-L})]\text{BF}_4$:

(MF = $\text{RhC}_{48}\text{H}_{40}\text{N}_5\text{P}_2\text{SCl BF}_4$)
 Found (%) : C = 57.22; H = 4.01; N = 7.01;
 Rh = 10.35
 Calculated(%) : C=57.29; H = 3.97; N = 6.96;
 Rh = 10.24

Preparation of $[\text{RhX}(\text{P}\phi_3)(\text{CO})(\text{ligand})]$ (X = Cl / Br)

These complexes were prepared using precursor complexes $[\text{Rh}(\text{CO})(\text{P}_3)_2\text{X}]$ (X = Cl / Br) following our previous method⁴.

Sl. No. 5 : $[\text{RhCl}(\text{P}\phi_3)(\text{CO})(\text{P-CH}_3\text{-L})]$:

(MF = $\text{RhC}_{27}\text{H}_{23}\text{N}_4\text{O P S Cl}$)
 Found (%) : C = 52.31; H = 3.78; N = 9.11;
 Rh = 16.66
 Calculated(%) : C=52.21; H = 3.70; N = 9.02;
 Rh = 16.59

Sl. No. 6: $[\text{RhCl}(\text{P}\phi_3)(\text{CO})(\text{P-Cl-L})]$:

(MF = $\text{RhC}_{26}\text{H}_{20}\text{N}_4\text{OP S Cl}$)
 Found (%) : C = 48.56; H = 3.50; N = 8.72;
 Rh = 16.15
 Calculated(%) : C=48.67; H = 3.12; N = 8.73;
 Rh = 16.06

Sl. No. 7 : $[\text{RhCl}(\text{P}\phi_3)(\text{CO})(\text{P-CH}_3\text{O-L})]$:

(MF = $\text{RhC}_{27}\text{H}_{23}\text{N}_4\text{O}_2\text{P S Cl}$)
 Found (%) : C = 51.11; H = 3.68; N = 8.68;
 Rh = 16.11

Calculated(%) : C=50.90; H = 3.61; N = 8.79;
Rh = 16.18

Sl. No. 8: [RhCl(Pφ₃)(CO)(P-CH₃CH₂O-L)] :

(MF= RhC₂₈H₂₅N₄OPS)

Found (%) : C = 51.21; H = 3.89; N = 8.36;
Rh = 15.82

Calculated(%) : C=51.65; H = 3.84; N = 8.60;
Rh = 15.83

Sl. No. 9: [RhBr(Pφ₃)(CO)(P-Cl-L)] :

(MF= RhC₂₆H₂₀N₄PSClOBr)

Found (%) : C = 45.55; H = 4.98; N = 8.01;
Rh = 14.98

Calculated(%) : C=45.51; H = 2.91; N = 8.16;
Rh = 15.02

Preparation of [RhX(Pφ₃)₂(ligand)] :

(X = Cl, Br, I, NCS, SnCl₃)

These complexes were prepared by adopting the similar process as reported by us in the literature⁵.

Sl. No. 10: [RhCl(Pφ₃)₂(P-CH₃-L)] :

(MF= RhC₄₄H₃₈N₄P₂SCl)

Found (%) : C = 61.76; H = 4.48; N = 6.32;
Rh = 11.42

Calculated(%) : C=61.79; H = 4.44; N = 6.22;
Rh = 11.45

Sl. No. 11: [RhBr(Pφ₃)₂(P-CH₃-L)] :

(MF= RhC₄₄H₃₈N₄P₂SBr)

Found (%) : C = 58.66; H = 4.21; N = 6.23;

Rh = 11.50

Calculated(%) : C=58.73; H = 4.22; N = 6.22;
Rh = 11.45

Sl. No. 12: [Rh(NCS)(Pφ₃)₂(P-CH₃-L)] :

(MF= RhC₄₅H₃₈N₅S₂P₂)

Found (%) : C = 61.52; H = 4.08; N = 7.77;
Rh = 11.82

Calculated(%) : C=61.57; H = 4.33; N = 7.98;
Rh = 11.74

Sl. No. 13: [Rh(SnCl₃)(Pφ₃)₂(P-CH₃-L)] :

(MF= RhC₄₄H₃₈N₄Cl₃SPSn)

Found (%) : C = 50.81; H = 3.74; N = 5.30;
Rh = 9.88

Calculated(%) : C=50.56; H = 3.64; N = 5.36;
Rh = 9.86

Elemental analysis were performed by micro analytical section of Regional Sophiscated Instrumentation centre, CDRI, Lucknow. IR spectra or ligands and complexes were recorded on a perkin-Elmer 577 spectrophotometer in the range of 4000-200 cm⁻¹ as KBr pellets and Electronic spectra on a beckmann DU-6, spectrophotometer. The ¹H NMR and ³¹P NMR spectra were recorded on Bruker 400 MHz or Varian FX 90 Q instruments using TMS and orthophosphoric acid as references respectively. The magnetic moment were measured on a gouy balance using Hg[CO(SCN)₄] as calibrant. The molar conductance of complexes (10⁻³ M) were measured in DMF using Wiss-Wekstatter weithein obb type LBR conductivity meter.

Results and Discussion

All isolated products are non-

hygroscopic stable solid and soluble in DMF, DMSO and other coordinating solvents. The addition of pyridine to methanolic solution of $[\text{RhCl}(\text{P}\phi_3)_2(\text{ligand})]$ followed by metathetical reaction with NH_4BF_4 yield corresponding derivative $[\text{RhCl}(\text{P}\phi_3)_2(\text{Py})(\text{ligand})]\text{BF}_4$. The other complexes were prepared by ligand substitution in precursors without change in oxidation state of rhodium. However, oxidation state of rhodium in complexes were verified by titrating the complexes with ceric ammonium sulphate using ferroin as indicator⁶. The complexes were titrated for two electron charge. All complexes were diamagnetic indicating univalent rhodium (Rh^+) and iso-structural with precursors and are four coordinated square planar⁷. These observations are in agreement with our previous work⁸ observed for other thioamide ligands. Electronic Spectrum of $[\text{RhCl}(\text{P}\phi_3)_2(1\text{Pt5TH})]$ exhibit three bands at 13840, 18340 and 23720 cm^{-1} . The first band (13840 cm^{-1}) is broad and weak while at 18340 cm^{-1} and 23720 cm^{-1} are medium intensity bands. The first band may be due to spin forbidden $^1\text{A}_{1g} \rightarrow ^3\text{A}_{2g}$ transition. The other band at 18340 cm^{-1} may be due to spin allowed $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition. The ligand (1Pt5TH) absorbs around 23710 cm^{-1} , so the third band (23720 cm^{-1}) could not be assigned. Thus, all four coordinated Rh(1) complexes are iso-structural with precursors.

IR Spectra :

A comparison of the IR spectral bands of the ligands and complexes indicate the formation of Rh-s bond (Table-1). Thioamide band IV mainly due to $\nu\text{C}=\text{S}$ mode under-

goes red shift of 25-50 cm^{-1} in all complexes suggesting bonding through thiocarbonyl sulphur of ligand⁹⁻¹¹. The systematic shift of other thioamide bands of ligands also support bonding through thiocarbonyl sulphur. The bonding through imino nitrogen was ruled out considering blue shift ($\sim 15 \text{ cm}^{-1}$) of thioamide bond I and $n\text{NH}$ (3050 cm^{-1}) of ligands. Bonding through sulphur is further supported by the presence of new bands at 345 cm^{-1} (vasym Rh-S), 335 cm^{-1} (vsym Rh-S) and at 385-379 cm^{-1} ($\nu\text{Rh-P}$) in far IR spectra of complexes. Moreover, the presence of single Rh-P stretching mode indicate two $\text{P}\phi_3$ group at trans-disposition in square planar structure.

All the characteristic bands of $\text{P}\phi_3$, Pyridine and CO group have been observed in the spectra of complexes¹²⁻¹⁴. The bands due to counter anion were observed at Ca. 1100 cm^{-1} for BF_4^- and presence of coordinated anions are confirmed at 2120 cm^{-1} (νCN), 830 cm^{-1} (νCS), 482 cm^{-1} (δNCS) for terminal NCS group¹⁵ and at 450 cm^{-1} and 435 cm^{-1} for SnCl_3^- group¹⁶.

^1H NMR and ^{31}P NMR spectra :

The metal ligand bonding is further substantiated by ^1H NMR and ^{31}P NMR spectra (Sl. no. 5 & 11). The complexes display signals in the δ 8.12–8.80 PPM range due to aromatic proton of $\text{P}\phi_3$ ¹⁷. The broad multiplet in the region δ 7.45 to δ 7.72 PPM due to phenyl protons of the ligand. The broad nature of peak may be probably due to large quadrupole resonance broadening effect of tetrazole nitrogen

Table 1. IR spectral Bands of ligands and complexes.

Compounds*	Thioamide Bands ψ				ν NH	ν Rh-S
	Band I	Band II	Band III	Band IV		
P-CH ₃ -L(C ₈ H ₈ N ₄ S)	Band I 500(m)	Band II 1280(s)	Band III 1044(m)	Band IV 810(m)	3050 (m)	
[Rh(P ϕ ₃) ₂ (Py)(P-CH ₃ -L)]BF ₄	1510(m)	1290(m)	1030(m)	785(m)	3060(m)	345 w 335 w
[RhCl(P ϕ ₃)(CO)(P-CH ₃ -L)]	1515(m)	1292(m)	1020(m)	780(m)	3070(m)	345 w 340 w
[RhCl(P ϕ ₃) ₂ (P-CH ₃ -L)]	1510(m)	1290(m)	1010(m)	785(m)	3065(s)	345 w 336 w
[RhBr(P ϕ ₃) ₂ (P-CH ₃ -L)]	1509(s)	1285(m)	1015(m)	780(m)	3070(s)	345 w 330 w
[Rh(NCS)(P ϕ ₃) ₂ (P-CH ₃ -L)]	1515(s)	1290(m)	1010(m)	780(m)	3100(m)	340 w 335 w
[Rh(SnCl ₃)(P ϕ ₃) ₂ (P-CH ₃ -L)]	1510(s)	1285(m)	1010(m)	782(m)	3110(m)	342 w 330 w
P-CH ₃ O-L (C ₈ H ₈ ON ₄ S)	1505(s)	1290(s)	1050(m)	800(m)		-
[Rh(P ϕ ₃) ₂ (Py)(CH ₃ O-L)]BF ₄	1510(m)	1280(m)	1020(m)	780(m)	3100(mb)	340 w 330 w
[RhCl(P ϕ ₃)(CO)(CH ₃ O-L)]	1515(m)	1278(m)	1010(m)	770(m)	3110(mb)	342 w 331 w
CH ₃ CH ₂ O-L (C ₉ H ₁₀ N ₄ OS)	1515(s)	1285(m)	1060(m)	805(m)	3100(m)	-
[Rh(P ϕ ₃) ₂ (Py)(P-CH ₃ CH ₂ O-L)]BF ₄	1510(s)	1275(m)	1020(m)	790(m)	3120(mb)	340 w 330 w
[RhCl(P ϕ ₃)(CO)(P-CH ₃ CH ₂ O-L)]	1515(s)	1270(m)	1010(m)	785(m)	3120(mb)	342 w 332 w
P-Cl-L (C ₇ H ₅ N ₄ SCI)	1498(s)	1280(s)	1055(m)	780(m)	3100(mb)	-
[Rh(P ϕ ₃)(Py)(P-Cl-L)]BF ₄	1505(s)	1290(m)	1020(m)	745(m)	3110(mb)	340 w 330 w
[RhCl(P ϕ ₃)(CO)(P-Cl-L)]	1510(m)	1280(m)	1010(m)	740(m)	3120(mb)	340 w 320 w
[RhBr(P ϕ ₃)(CO)(P-Cl-L)]	1510(m)	1275(m)	1015(m)	745(m)	3130(mb)	342 w 325w

* : L = 1-Phenyl tetrazoline-5thione (C₇H₅N₄S); ψ = Band I (δ NH + δ CH + ν C=N);Band II (ν C-N + δ NH + δ CH + ν C=S);Band III (ν C \equiv N + ν C \equiv S); Band IV (ν C \equiv S)

atoms or ligand exchange reaction occurring in solution. The methyl proton and imino protons resonances in complexes are observed at δ 2.4 PPM and δ 1.2 PPM respectively indicating absence of deprotonation in complexes.

The ^{31}P NMR spectra of $[\text{RhCl}(\text{P}\phi_3)_2(\text{P}-\text{CH}_3-\text{L})]$ was recorded in order to confirm the presence of $\text{P}\phi_3$ group and to determine the geometry of the complex. The appearance of signal around 23.70 – 28.70 in the spectrum of complex confirmed the presence of magnetically equivalent phosphorus atoms and suggesting that the two $\text{P}\phi_3$ groups are trans to each other¹⁸. Thus, ^1H NMR and ^{31}P NMR spectral observations are consistent with the conclusions drawn from IR spectral results.

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